PB89-118376

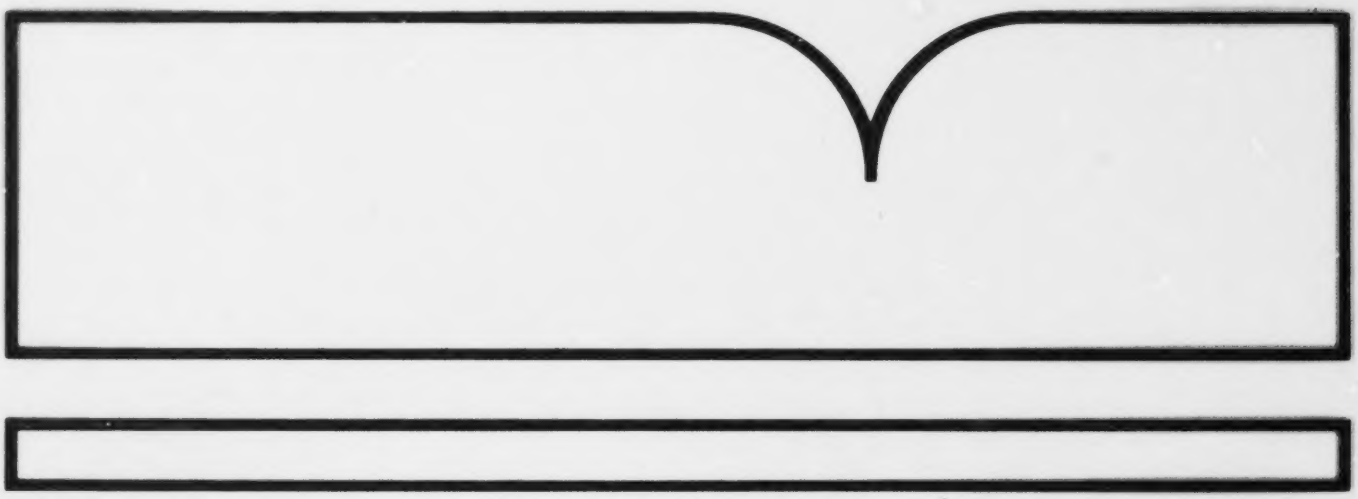
Comparison of Techniques for Measurement of Ambient Levels of Hydrogen Peroxide (Journal Version)

Northrop Services, Inc.
Research Traingle Park, NC

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

1987



U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA (Please read Instructions on the reverse before comple		
1. REPORT NO. EPA/600/J-88/159	2.	3 PB89-118376
4. TITLE AND SUBTITLE COMPARISON OF TECHNIQUES FOR MEASUREMENT OF AMBIENT LEVELS OF HYDROGEN PEROXIDE (Journal Version)		5. REPORT DATE 1988 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) T. E. Kleindienst, P. B. Shepson, D. N. Hodges, C. M. Nero, R. R. Arnts, P. K. Dasgupta, H. Hwang, et al.		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Northrop Services Inc., RTP, NC 27707 ASRL, RTP, NC 27711 Texas Tech University, Lubbock, TX 79409 etc.		10. PROGRAM ELEMENT NO. N104/L/05/05 - 6128 (FY-88) 11. CONTRACT/GRANT NO. 68-02-4033 68-02-4443
12. SPONSORING AGENCY NAME AND ADDRESS Atmospheric Sciences Research Laboratory-RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711		13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA/600/09
15. SUPPLEMENTARY NOTES Environmental Science & Technology, 22(1):53-61, Jan. 1988		

16. ABSTRACT

A study was conducted to measure hydrogen peroxide (H_2O_2) from three sources: (1) zero air in the presence and absence of common interferences, (2) steady-state irradiations of hydrocarbon/NO_x mixtures, and (3) ambient air. The techniques employed for measuring H_2O_2 included infrared absorption from a diode laser, fluorescence from an enzymatically produced complex, and chemiluminescence from reaction with luminol. Four systems, each of which utilized one of the above techniques, were compared with respect to sensitivity, selectivity, and dynamic range in measuring H_2O_2 conentrations ranging from 0.062 to 128 ppbv. For pure samples measured in zero air, agreement of 14 to 23% was achieved when compared to standard values. In these samples there was no indication of interferences for an H_2O_2 level of 6 ppbv except in the luminol technique where a negative interference was caused by SO_2. Agreement among techniques was much worse for measurement of H_2O_2 produced in the photochemical mixtures (irradiated CH_3CHO/NO_x and C_2H_4/NO_x). Significant concentrations of organic peroxide were measured by the enzymatic techniques. During ambient monitoring the techniques employed showed quantitative agreement with the mean values with an overall average deviation of 30%.

(Copyright (c) 1987 American Chemical Society)

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED 20. SECURITY CLASS (This page) UNCLASSIFIED	21. NO. OF PAGES 12 22. PRICE

EPA Form 2220-1 (9-73)

EPA/600/J-88/159
JOURNAL ARTICLE

Reprinted from ENVIRONMENTAL SCIENCE & TECHNOLOGY, Vol. 22, Page 53, January 1988
Copyright © 1987 by the American Chemical Society and reprinted by permission of the copyright owner.

Comparison of Techniques for Measurement of Ambient Levels of Hydrogen Peroxide

Tadeusz E. Kleindienst,* Paul B. Shepson, Dennis N. Hodges, and Chris M. Nero

Northrop Services, Inc.—Environmental Sciences, Research Triangle Park, North Carolina 27709

Robert R. Arnts

Atmospheric Science Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711

Purnendu K. Dasgupta and Hoon Hwang

Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409

Gregory L. Kok, John A. Lind, and Allan L. Lazrus

National Center for Atmospheric Research,† Boulder, Colorado 80307

Gervase I. Mackay, Laura K. Mayne, and Harold I. Schiff

Unisearch Associates, Concord, Ontario, Canada L4K 1B5

■ A study was conducted to measure hydrogen peroxide (H_2O_2) from three sources: (1) zero air in the presence and absence of common interferences, (2) steady-state irradiations of hydrocarbon/NO_x mixtures, and (3) ambient air. The techniques employed for measuring H_2O_2 included infrared absorption from a diode laser, fluorescence from an enzymatically produced complex, and chemiluminescence from reaction with luminol. The measurements were conducted simultaneously from a common manifold. Four systems, each of which utilized one of the above techniques, were compared with respect to sensitivity, selectivity, and dynamic range in measuring H_2O_2 concentrations ranging from 0.062 to 128 ppbv. For pure samples measured in zero air, agreement of 14–23% was achieved when compared to standard values. In these examples, there was no indication of interferences for an H_2O_2 level of 6 ppbv except in the luminol technique where a negative interference was caused by SO_2. Agreement among techniques was much worse for measurement of H_2O_2 produced in the photochemical mixtures (irradiated CH_3CHO/NO_x and C_2H_4/NO_x). In these mixtures, significant concentrations of organic peroxide were also measured by the enzymatic techniques. For the ambient measurements, the techniques employed showed quantitative agreement with the mean values with an overall average deviation of 30%. This study demonstrates a systematic approach for conducting an intercomparison among the four techniques whereby increasingly complex mixtures containing H_2O_2 are used to help determine the nature of interfering species and the concentrations that lead to divergent results.

Introduction

Hydrogen peroxide (H_2O_2), an oxidant formed in the atmosphere, has recently been the subject of intense scrutiny. Produced from the recombination of hydroperoxyl radicals, H_2O_2 is extremely soluble in water and has a Henry's law constant of 1.5×10^5 M atm^{-1} at 25 °C. It is currently believed that H_2O_2 is the primary species in the atmosphere that oxidizes sulfur(IV) compounds to sulfur(VI) in the condensed phase (*1*). This has been suggested not only because of the high aqueous solubility of H_2O_2 but also because its rate of reaction with sulfur(IV) increases with increasing acidity. To quantitatively assess the role of H_2O_2 in this process, accurate measurements of H_2O_2 in the gas and aqueous phases need to be obtained.

Until recently, few reliable measurements of atmospheric gas-phase H_2O_2 concentrations were made because no sensitive technique free of interferences had been found. One study conducted by Bufalini et al. (*2*) in Riverside, CA, suggested that extremely high levels of H_2O_2 (as high as 180 ppbv) could be produced under conditions that give rise to high O_3 levels. A later study by Kok et al. (*3*) conducted in Claremont and Riverside, CA, indicated that ambient levels of H_2O_2 were considerably lower (~20 ppbv) under similar conditions of high O_3 concentrations. In that study, the H_2O_2 concentrations measured with $TiSO_4$, $TiCl_4$, and luminol (vide infra) showed poor correlation, albeit both titanium methods were operated near their detection limits.

The results of these studies, which were based on field measurements, point out the necessity of conducting carefully controlled laboratory intercomparison studies. By producing surrogate mixtures from the very simple to the very complex, sources of discrepancies among techniques can be more easily evaluated. The study described in this paper represents such an intercomparison study for H_2O_2. This study was conducted to measure H_2O_2 in zero air with and without interferences, in surrogate photochemical mixtures, and in ambient air. Four techniques for measuring H_2O_2 (three of which were recently developed) are compared with respect to sensitivity, selectivity, and dynamic range.

Experimental Section

This intercomparison study was conducted at Northrop Services, Inc.—Environmental Sciences (NSI-ES), Research Triangle Park, NC, during the period June 16–26, 1986. Participants in the study included groups from the National Center for Atmospheric Research (NCAR), Boulder, CO; Texas Tech University (TTU), Lubbock, TX; Unisearch Associates, Inc., Toronto, Ontario, Canada; and NSI-ES. The techniques employed by each of the groups to measure H_2O_2 are summarized below with extended descriptions given by reference to each laboratory's publications.

Analytical Methods. (1) NCAR. NCAR employed a continuous-scrubbing, fluorometric detection (CSFD) technique described by Lazrus et al. (*4*, *5*). The CSFD technique uses a mixed flow of air and aqueous solution

†The National Center for Atmospheric Research is sponsored by the National Science Foundation.

NTIS is authorized to reproduce and sell this report. Permission for further reproduction must be obtained from the copyright owner.

© 1987 American Chemical Society

to extract gas-phase peroxides into aqueous solution. The resulting solution is analyzed for peroxides by an enzymatic technique. In this procedure, the dimer of *p*-hydroxyphenylacetic acid is formed quantitatively through the reacton of peroxides, *p*-hydroxyphenylacetic acid, and the enzyme peroxidase. The concentration of the dimer is determined by fluoresence spectroscopy, and is linearly related to the total peroxide concentration in solution. Under normal operating conditions, the collection efficiency for H_2O_2 is 100%. The collection efficiency for methyl hydroperoxide is about 60%, and the collection effficiency for organic hydroperoxides larger than C_1 is much smaller.

To discriminate between H_2O_2 and organic hydroperoxides, a dual-channel analytical approach is used. In one channel, the total hydroperoxide concentration is measured. In the other channel, the enzyme catalase, which reacts rapidly with H_2O_2, is used to remove the H_2O_2 and leave the organic hydroperoxides for analysis. The net concentration of H_2O_2 is determined by the difference between the two channels. The accuracy of this discrimination of peroxides by catalase is dependent on the type of organic hydroperoxide present and the concentration relative to H_2O_2. Catalase reactivity for the destruction of hydroperoxides decreases significantly as the R group on the hydroperoxides increases in size. Under the conditions of the analytical technique, essentially no destruction of organic hydroperoxides takes place if the R group is C_2 or higher. For C_1 hydroperoxides, the reaction with catalase is sufficiently slow that only small errors are introduced if the concentration of C_1 hydroperoxides is less than 20% of the total H_2O_2 concentration (*4*). When the concentration of C_1 hydroperoxides increases to several times that of the H_2O_2 present, the reaction of catalase with C_1 hydroperoxides amounts to about 20%, and this appears as H_2O_2 in the final calculation. When high concentrations of C_1 hydroperoxides are expected, an independent calibration needs to be made with a C_1 hydroperoxide to assess the amount of reaction with catalase.

The system is calibrated with aqueous standards of H_2O_2. The stock standard is certified by titrating against standard $KMnO_4$, which is standardized against sodium oxalate. The working standards of H_2O_2 are prepared by serial dilution of the stock standard. A full multipoint instrument calibration was performed at the beginning of each sampling day, and point calibration checks were done at regular intervals. A limited number of calibrations were performed with methyl hydroperoxide to check the response between the two channels and to assess the removal of methyl hydroperoxide by catalase.

(2) TTU. TTU employed a diffusion-scrubbing, fluorescence detection (DSFD) technique similar to that outlined in the literature (*6–8*). The approach uses essentially the same analytical chemistry as that of NCAR method, with differences in the detailed approach. Sample collection is achieved with the use of microporous tubing through which the scrubbing solution flows. The airstream, which is confined to flow along the outer wall of the microporous tubing, has free access to the scrubbing solution, and the soluble gas components dissolve into it. The reaction of H_2O_2 with *p*-hydroxyphenylacetic acid in the presence of peroxidase to form a fluorescent dimer occurs downstream at pH 6.5. Following this reaction, the pH of the solution is rapidly raised, without dilution, to 9.5 by using NH_3. The efficiency for fluorescence is increased at the higher pH (*7*). To differentiate between the organic and inorganic hydroperoxide, an MnO_2-packed reactor incorporated in the loop of a switchable six-port valve was used to selectively remove H_2O_2 from the sampling stream. It was previously determined that MnO_2 is extremely inefficient in removing CH_3OOH and higher peroxides such as *tert*-butyl hydroperoxide, peroxyacetic acid, and benzoyl peroxide (*8*); however, the extent to which MnO_2 might remove other low molecular weight organic hydroperoxides is unknown. Because H_2O_2 concentration is determined by difference (total hydroperoxide – organic hydroperoxide), only an upper limit can be determined in the presence of an organic peroxide that has not been individually evaluated by the technique (i.e., any removal of organic peroxide by MnO_2 will be reflected in a systematically higher value for H_2O_2).

The system is calibrated for H_2O_2 by use of a gas calibration system. Microporous tubing is immersed in a thermostated solution standard of H_2O_2 in water. Air passing through the tubing collects a fixed mass of H_2O_2, and the concentration is determined by the Henry's law constant (*9*).

(3) Unisearch, Inc. Unisearch employed tunable diode laser absorption spectrometry (TDLAS) for the direct measurement of gas-phase H_2O_2 (*10*). The tunable diode laser operates in the region 5–20 μm and has a line width much smaller than a Doppler-broadened vibrational rotational line for H_2O_2. The extremely narrow line width permits high selectivity. To minimize line jitter, the laser scans the absorption line repeatedly. This approach serves to cancel background noise (because of its random character) and allows measurements of absorbances better than 10^{-5}. Absorption of H_2O_2 occurs within a White cell that has a base path of 150 cm and operates at about 25 Torr to minimize pressure broadening of individual lines. The multiple pass cell yields effective path lengths of 150 m.

In actual operation, the incident laser power is not measured because extinction coefficients for individual vibrational rotational lines are generally not known for most compounds. Thus, the system is calibrated by introducing a known concentration of gas-phase H_2O_2 (in N_2) at the sample inlet. The calibration source used in the Unisearch experiment is a permeation system, with the H_2O_2 output determined by a $TiCl_4$ technique (vide infra). This approach effectively accounts for any first-order loss process in the inlet system.

(4) NSI-ES. NSI-ES employed the luminol technique for the measurement of H_2O_2. It has been previously reported that, since this technique uses glass impingers, it suffers both positive (*11*, *12*) and negative (*11*) artifacts with O_3. A negative interference has also been observed with SO_2 (*12*). The procedures employed by this technique were largely the same as those originally described (*13*). Air samples are taken by impinger collection in water at 0 °C. Because of its high Henry's law constant, the collection efficiency for H_2O_2 is virtually 100% at a sampling rate of 1 L min^{-1}. Total air volumes are generally 30 L. Solutions containing the analyte H_2O_2 (or standard), luminol, and cupric ion as catalyst, all at pH 12.8, are mixed in a light-tight cell with a peristaltic pump. Upon mixing the solutions, chemiluminescent products are produced, and the emitted radiation is detected in a photomultiplier tube. A sample loop is employed to yield reproducible injections, and the signal is measured as the integrated output from the photomultiplier.

The system is calibrated with solutions produced by serial dilution of a stock solution. The diluted standards were made daily and stored in PFA Teflon containers. The concentration of the H_2O_2 stock solution is determined by titration against $KMnO_4$, which itself has been standardized against sodium oxalate (an NBS oximetric standard).

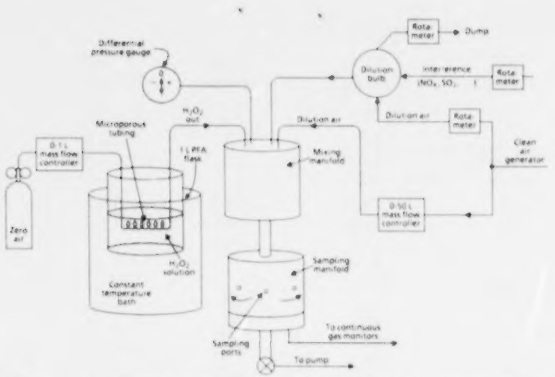


Figure 1. Generation system for H_2O_2 standards in zero air with and without added interferences.

The water used in sample collection and standards production was doubly deionized and distilled, with H_2O_2 levels in the freshly treated (blank) water generally less than the 100 nM detection limit of the instrument.

Experimental Procedures. In the first phase of the study, pure standards of H_2O_2 were generated and mixed with zero air. Vapor-phase H_2O_2 was generated by passing zero air through microporous tubing immersed in a solution of H_2O_2 in water. At the flow rates employed (up to 1 L min^{-1}), the gas-phase concentration of H_2O_2 emanating from the generator could be continuously maintained at its Henry's law constant concentration. To maintain short-term stability, the generator was immersed in a thermostated bath. The H_2O_2 concentration derived from the generator was solely dependent on the bath temperature and the solution molarity (*9*, *14*). The concentrated H_2O_2 gas stream was fed into a 1-L manifold where it was diluted with zero air at 30 L min^{-1}. This air was purified (O_3, CO, NO_x < 1 ppbv; HC < 50 ppbC) with the use of an Aadco pure air generator although CO_2 was not removed. The air flowing through the generator was regulated with a mass flow controller (FC 360, Tylan Corp.), and the dilution air was regulated by use of 3–50 L min^{-1} (Teledyne-Hastings) mass flow controller. Each controller was calibrated against a bubbler flow meter or calibrated dry test meter prior to use. Excess effluent was pumped away to maintain the manifold system within 2 Torr of atmospheric pressure, ensuring quantitative transfer from the H_2O_2 generator.

The diluted mixture was fed directly into a second manifold where sampling took place. The generators, manifolds, and connecting lines were all shielded from light and were constructed of PFA Teflon, which proved to be extremely inert with respect to wall removal of H_2O_2. A schematic of the generation and dilution system is shown in Figure 1.

The gas samples used to generate pure standards of H_2O_2 were standarized with $TiCl_4$ (*15*). Upon reaction with H_2O_2, $TiCl_4$ forms a yellowish complex, which has a maximum absorbance at 415 nm. The extinction coefficient of the complex at this wavelength was measured with dilute standard solutions of H_2O_2, in a concentration range of 0.1–2 mM. These standards were made from the stock solution used to calibrate the luminol apparatus. The calibration curve yielded an extinction coefficient of 739 M^{-1} cm^{-1} at 415 nm. This value compares very well with the extinction coefficient of 735 M^{-1} cm^{-1} obtained by Pilz and Johann (*15*).

Undiluted, vapor-phase H_2O_2 concentrations from the generator were determined by impinger collection through a 28 mM solution of $TiCl_4$ at pH 1. These calibrations were performed daily during the study. Two generators were used; one contained a 1.0 M H_2O_2 solution and the other, a 0.010 M H_2O_2 solution. At a bath temperature of 16 °C, the high-concentration generator produced ~6 ppmv gas-phase H_2O_2 and the second generator, 60 ppbv. With use of the dilution factors, the former generator yielded accurate concentrations in the range 5–200 ppbv and the latter, 0.05–2 ppbv. Over an entire sampling period the variability of the flows, bath temperature, and solution concentration was less than 2%. This value probably reflects the stability of the generator during a single sampling period.

By use of this technique for generating standards, the estimated uncertainty was approximately 10%. The largest source of uncertainty in this estimate was the calibration of the Ti complex, a 5–10% uncertainty. Other sources of uncertainty (the collection efficiency of H_2O_2 in the $TiCl_4$ solution, the flow calibrations, the transfer from the generator to the mixing manifold, and the absorbance measurement) were much less than 5% each. However, the possibility of wall loss in the manifold system needed to be evaluated experimentally. This was done prior to the study by comparing the expected concentration from the generator and its dilution factor with measured values obtained by the luminol technique. Although this technique is near its detection limit in the range 1–5 ppbv, within the reproducibility of the measurements no significant wall losses were observed. This observation was subsequently supported during the course of the study. In light of the 4-s residence time for the effluent in the manifold, this result is not surprising.

Several experiments were performed with a second dilution system in which one or more interferences were added quantitatively to the mixing manifold (Figure 1). The interferences included common atmospheric pollutants: nitrogen dioxide (NO_2), sulfur dioxide (SO_2), ozone (O_3), and formaldehyde (HCHO). NO_2 and SO_2 were taken from concentrated tank mixtures (1% in N_2), prediluted with zero air, and added to the mixing manifold. O_3 was generated by passing pure oxygen through an electrical discharge generator. Concentrated ozone was scrubbed of H_2O_2 by passing the airstream through deionized/distilled water then was diluted and added to the mixing manifold. HCHO was generated by bubbling zero air through a dilute formalin solution. Methyl hydroperoxide (CH_3OOH), a minor component of polluted atmospheres, was also employed as an interference. A solution of CH_3OOH in water (supplied by NCAR) was produced as described by Lind and Kok (*14*). This compound was added to the mixing manifold directly in a generation system identical with that for H_2O_2. The concentrations of the inorganic compounds were measured directly from the sampling manifold by continuous gas monitors, and HCHO was measured from the sampling manifold by impinger collection in 2,4-dinitrophenylhydrazine (DNPH) (*16*). The CH_3OOH concentration was calculated from the Henry's law constant (*14*) at the temperature of the bath (16 °C), the solution concentration, and the dilution factor.

In the second phase of the intercomparison study, gas mixtures [ethylene (C_2H_4)/NO_x and acetaldehyde (CH_3CHO)/NO_x] were irradiated in a smog chamber, which was operated in a dynamic mode. The utility of this type of procedure has already been demonstrated in a previous intercomparison study (*17*). These dynamic systems provide stable concentrations of H_2O_2 in the presence of many organic and inorganic species found in polluted air, including (for the CH_3CHO/NO_x irradiation) peroxyacetyl nitrate (PAN). Details of the smog chamber

Table I. Comparison of Techniques for Measuring H_2O_2 in Zero Air (ppbv, Except Where Indicated)

sample period	conditions	$[H_2O_2]^a$ standard	NCAR (CSFD)	TTU (DSFD)	UNI (TDLAS)	NSI-ES (LUM)	$[H_2O_2]^b$ mean
A1	c	12.1	–[d]	7.3	11.4	9.9	9.53
A2		1.1	1.4	1.3	1.2	2.4	1.58
A3		0.11	–	0.19	0.07	–	0.130
A4		0.34	0.43	0.43	0.41	–	0.423
A5		12.5	13.9	9.4	14.0	18.0	13.8
A6	RH = 65%	12.8	9.0	9.5	11.5	16.6	11.7
A7		128	135	70	116	148	117
B1[e]	zero air	0	0.06	0[f]	0	–	na[g]
B2[e]	$[O_3]$ = 456	0	0.08	0.82	0	–	na
B3	$[O_3]$ = 414	6.4	4.8	–	5.0	6.7	5.50
B4	$[O_3]$ = 118	6.6	5.2	–	5.4	6.2	5.60
B5	$[SO_2]$ = 32	6.5	5.9	–	5.7	0[e]	5.80
C1	$[SO_2]$ = 6	6.4	6.7	5.5	7.0	4.9[e]	6.40
C2	$[NO_x]$ = 125	6.6	7.1	6.0	6.6	6.0	6.43
C3		6.6	7.2	6.5	7.1	6.2	6.75
C4	[HCHO] = 18	6.7	7.8	7.0	8.2	6.5	7.38
C5	[HCHO] = 18 $[SO_2]$ = 19	6.5	7.8	6.5	6.9	0.6[e]	7.07
C6	[HCHO] = 18 $[SO_2]$ = 9 $[O_3]$ = 161	6.6	7.8	6.8	6.8	8.1[e]	7.13
C7	[HCHO] = 58	6.6	8.1	6.3	7.9	6.2	7.13
F2		0.12	0.14	0.15	0.12	–	0.137
F3		0.062	0.083	0.070	0[e]	–	0.077
F4[e]	zero air	0	0	0	0	–	na
G2	$[CH_3OOH]$ = 7	8.2	8.0	5.3	7.0	6.5	6.70
av percent deviation from standard			18.3	21.4	14.3	23.4	13.1
av percent deviation from mean			9.7	16.1	9.3	19.2	–

[a] Standard from $TiCl_4$ determination and dilution factor. [b] Mean value taken from the average of the four techniques. [c] Absence of notation indicates H_2O_2 in zero air. [d] Data not taken. [e] Data not included in mean (see text for criterion). [f] All zero values indicate H_2O_2 below detectable limit. [g] na = not applicable.

and the associated instrumentation have already been presented (*18*). The effluent from the smog chamber passed through a 6-m length of 19-mm PFA tubing shielded from sunlight and connected directly to the mixing manifold. The residence time in this line was approximately 3 s. The pressure in the sampling manifold was maintained slightly below that in the reaction chamber ensuring efficient transfer of the effluent.

In the third phase of the study, ambient sampling of Research Triangle Park, NC, air was performed for 14 h on the nights of 21, 22, and 23 June 1986 and for a 24-h period beginning at 1730, 24 June 1986. The sample port, which was located approximately 4 m above the ground, was connected to the mixing manifold with an 11-m segment of 19-mm tubing. Under normal operating conditions, the average residence time of ambient air in this line was approximately 5 s. As in the other cases, sampling was conducted from the sampling manifold (Figure 1), guaranteeing that the samples were taken from the same air mixture.

Results

H_2O_2 Mixtures in Zero Air. As indicated in the previous section, wall losses in the manifold system were minor. However, losses could occur in the lines connecting the manifold to the individual systems. Thus, sampling lines ($^1/_4$″) to the individual apparati were fabricated of PFA Teflon, and the lengths of the lines were adjusted to insure that the residence time of the effluent in the lines was the same in each system. Since the average residence time was less than 1 s, such line losses were not expected to be a source of systematic error for these measurements.

The data for each of the sampling periods in this phase of the study are given in Table I. Individual sampling periods were generally 1 h in length. Collection of NCAR samples involved continuous detection over the entire period while TTU, Unisearch, and NSI-ES samples were taken in a discrete measurement mode. In Column 1, individual letters (A, B, ...) represent sampling periods on different days. Column 2 shows the interferences added for individual sampling periods. For O_3, HCHO, and SO_2, several concentrations were employed; and in two of the runs (C5 and C6), multiple interferences were added simultaneously (e.g., sampling period C6 included H_2O_2, HCHO, SO_2, and O_3 in zero air).

Column 3 of Table I gives the standard values of H_2O_2 calculated from the $TiCl_4$ measurements of the concentrated gas samples and the known dilution factor. A minor correction (≤4%) was made to the standard value to account for systematic increases or decreases in the bath temperature. The magnitude of the correction was based on Henry's law.

The data for the sampling periods from each of the participating groups are given in columns 4–7 of Table I. In a few cases, samples were not taken because of instrument malfunction. Although the random error associated with each measurement is not given, the precision of each technique was not a significant factor in the uncertainty of the measurement.

The second to last row provides the average percent deviation with respect to the standard values. These average deviations range from 14% for Unisearch to 23% for NSI-ES. In the final column, mean values from the four groups are presented for each sampling period. (Each group's data are weighed equally.) Only those data that showed no systematic error due to interferences and were above the stated detection limits are used in the calculation of the mean values. For example, in sampling periods B5, C1, C5, and C6, the data from the luminol technique are not incorporated in the mean calculation since an interference due to the presence of SO_2 is apparent. Similarly, no Unisearch data are incorporated for mean H_2O_2 values

Table II. Concentrations of Major Chemical Species for the Photochemical Mixtures (ppbv)[a]

compd	F1 (CH_3CHO/NO_x), τ = 2.7 h	E1, E3, E4 (CH_3CHO/NO_x), τ = 6.7 h	G3, G4 (C_2H_4/NO_x), τ = 6.7 h
initial			
HC_0	913	879	979
NO_0	235	109	96
$(NO_2)_0$	53	116	112
final			
HC_τ	722	504	411
NO_τ	11	0	0
$(NO_x\text{–}NO)_\tau$	231	200	114
$(O_3)_\tau$	80	257	425
PAN_τ	111	200	–
$HCHO_\tau$	65	77	225

[a] Reaction chamber operated in a dynamic mode at indicated residence time τ.

less than 0.10 ppbv (e.g., sampling period F3). From the standard H_2O_2 values (column 3) and the mean H_2O_2 values (column 8), a percent deviation is calculated for each sampling period. For the 20 periods for which there is a comparison, the average deviation between the standard and mean values is 13%. However, the net deviation is only 3% (i.e., on average the mean was 3% higher than the standard; the net deviation is defined by

$$(1/n)\sum_{i=1}^{n}(x_i - x_{si})/x_{si}$$

where x_i is the measured value and x_{si} is the standard value for sample i given a total of n samples). This would indicate that systematic errors in the standard were probably very small.

In Figure 2, all data for H_2O_2 in zero air with no added interferences are plotted against the standard values. A log–log scale is employed to show the data covering 3.5 orders of magnitude on a single plot. All data for which the individual values coincide with the standard values lie on the line, which has a slope of unity.

Photochemical Mixtures. Three photochemical mixtures were used to generate small to moderate concentrations of H_2O_2 in the presence of many interferences. These mixtures are representative of the types of components expected to be found in urban atmospheres. Thus, the purpose of these measurements is to identify potential interferences and not to simulate atmospheric conditions. Steady-state concentrations of these mixtures were generated in a smog chamber operated in a dynamic mode. The extent of reaction for each of the mixtures was determined by the input concentration of the reactants, the radiation intensity, and the average residence time τ for gases in the chamber. The mixtures employed were (1) CH_3CHO/NO_x, small extent of reaction; (2) CH_3CHO/NO_x, large extent of reaction; and (3) C_2H_4/NO_x, large extent of reaction. By small extent of reaction, we refer

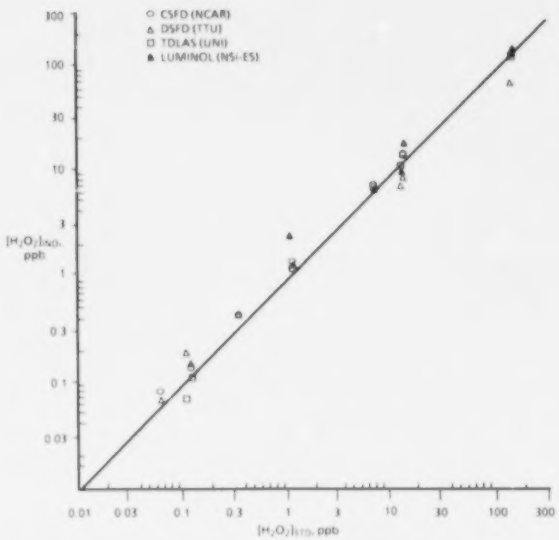


Figure 2. Comparison of measured H_2O_2 concentrations in zero air against the standard values. The standard H_2O_2 concentrations are given by points along the line. $[H_2O_2]_{IND}$ represents the individual H_2O_2 values.

to the fact that NO is present in the system at a high enough concentration to minimize formation of peroxides. (The fast reactions, HO_2 + NO and RO_2 + NO, insure that the HO_2 and RO_2 concentrations remain very low under these conditions.) A large extent of reaction indicates that the NO concentration is sufficiently low to allow significant gas-phase formation of peroxides.

One of the main objectives of employing the irradiated CH_3CHO/NO_x mixtures at two extents of reaction was to provide PAN as an interfering species in the presence and absence of H_2O_2. This technique also provided a variety of interferences simultaneously, and thus was expected to be more representative of a real air mass; the interference concentrations were more than 1 order of magnitude higher than ambient concentrations. Table II gives concentrations for the major chemical species, both reactant and product, present in the mixtures before and during the irradiation. These were measured according to analytical techniques previously described (*18*). The amount of reacted hydrocarbon is calculated from the difference between the initial and final concentrations. The mixtures were generated and maintained in the chamber for at least two residence times before sampling for peroxide occurred.

Table III presents the H_2O_2 and organic peroxide concentrations for these photochemical mixtures. (Organic peroxides were only measured by the techniques employing enzymatic reactions.) In both CH_3CHO systems, PAN was present at concentrations considerably higher than ambient levels. The CH_3CHO mixture at the short residence time (with NO present) was relatively simple, containing,

Table III. H_2O_2 and ROOH Concentrations (ppbv) for Photochemical Mixtures

sample	mixture (HC/NO_x)	$[H_2O_2]$, ppbv				[ROOH], ppbv[a]
		NCAR	TTU	UNI	NSI-ES	TTU
F1	CH_3CHO, τ = 2.7 h	0.30	0.34	0	2.2	3.2
E1, E3	CH_3CHO, τ = 6.7 h	1.6	0.6	1.1	3.9	8.6
E4	(+400 ppbv NO)	1.6	0.8	0.71	0.65	6.8
G3	C_2H_4, τ = 6.7 h	0.13	1.3	2.5	46.7	30
G4	(+22 ppbv SO_2)	0	0.7	2.5	27.4	33

[a] Concentration calculated assuming R = CH_3.

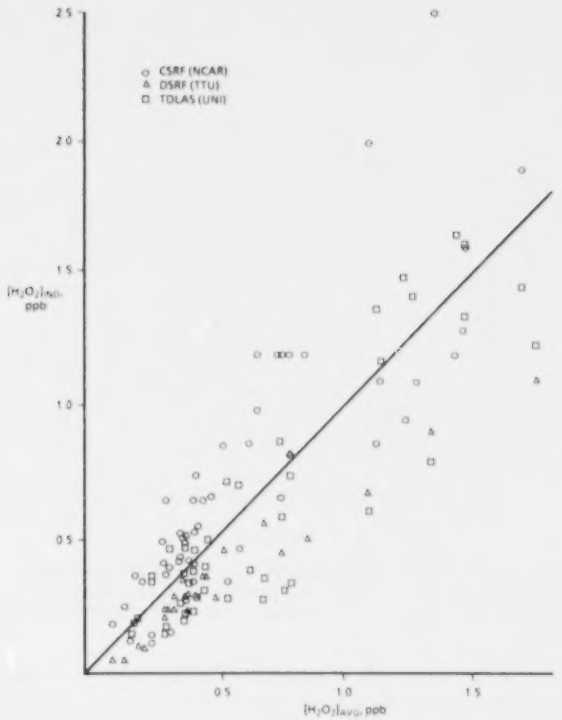


Figure 3. Measurements for H_2O_2 in ambient air. The line represents the mean values. Data are given for the two enzymatic methods and the absorption method.

in addition to residual CH_3CHO and NO_x, the major organic products HCHO, PAN, and CH_3ONO_2. At the long residence time, organic peroxides and other nitrates were formed. For the CH_3CHO/NO_x irradiation at the long residence time, a second experiment (E4) was performed whereby 400 ppbv of NO was instantaneously added to the mixture. NO served to remove O_3 and peroxy radicals (arising, for example, from the equlibrium $RO_2NO_2 \rightleftharpoons RO_2 + NO_2$) present in the system. Possible interferences from these two sources could then be checked. However, only a small fraction of PAN was, in fact, removed by the addition of NO. The C_2H_4/NO_x irradiation yielded products containing H_2O_2 with HCHO and inorganic compounds present. Unexpectedly, an unidentified organic peroxide was also detected in this system (vide infra). A second experiment (G4) was performed whereby SO_2 was added to the irradiated C_2H_4 mixture to determine the effect of SO_2 on the H_2O_2 measurement with a variety of other interferences present. Organic peroxides in the CH_3CHO as well as in the C_2H_4 system are also reported in Table III. (It should also be noted for the organic hydroperoxides that the collection efficiency in the enzymatic system is not necessarily unity; for purposes of calculation only, the collection efficiency and efficiency for removal by MnO_2 in the DSFD system were assumed to be equivalent to that of CH_3OOH.)

Ambient Samples. The data from the ambient samples are presented in Figure 3. The NSI-ES luminol measurements were not conducted for ambient samples because of the high detection limits. The data are plotted as the mean value against the individual values, and thus the scatter represents deviations from the mean. On average, the Unisearch (UNI) data were 15% lower, the TTU data 25% lower, and NCAR data 25% higher than the mean. When the data were paired, the correlation coefficient obtained from each pair gave 0.87 (NCAR–TTU), 0.78 (TTU–UNI), and 0.62 (NCAR–UNI). Although NCAR–TTU set yielded the best correlation, the slope of the derived curve showed the greatest deviation from unity.

Discussion

The intercomparison study was designed to systematically provide increasingly complex air mixtures containing H_2O_2 to help determine the nature of interfering species and the concentrations at which they lead to diverging results among the four techniques. For three of the techniques (TDLAS, DSFD, and CSFD), no interferences were observed in the zero air mixtures for O_3, SO_2, NO, NO_2, HCHO, and CH_3OOH at the levels tested. The luminol technique showed a negative interference for SO_2 at levels as low as 6 ppbv, which is representative of low to moderate ambient levels (*19*). However, it should be pointed out that this study was performed to survey potential interferences, and thus the possibility of interferences cannot be eliminated on a purely statistical basis. For the standard sample mixtures, the average deviation from the standard values for the four techniques ranged from 14 to 23%.

There was a wider discrepancy of the data for the photochemically generated mixtures. Although the concentrations of the reactant and products may have been high relative to ambient air, the data show the possibility of serious divergences in the presence of certain atmospheric components. For example, in the C_2H_4/NO_x irradiation for the four techniques, no two sets of values for the H_2O_2 concentration agree by better than a factor of 2. The luminol values are more than 1 order of magnitude higher than the other data. In this photochemical mixture, however, there appears to be a large organic component to the measured peroxide (according to the DSFD technique, 1 order of magnitude higher than the inorganic component). Since the inorganic component is determined by difference (total hydroperoxide – organic hydroperoxide), small relative errors in these two values could lead to potentially large errors in the calculation of the inorganic component. (Under ambient conditions in which the H_2O_2 concentration is higher than organic hydroperoxides, this uncertainty does not represent a serious consideration.)

The production of organic peroxides in the C_2H_4/NO_x system is largely unknown and has not been unambiguously demonstrated. It has been suggested (*20*) that the formation of hydroxymethyl peroxide, $HOCH_2OOH$ (HMP), could occur through the addition of water to the CH_2OO radical formed by the ozonolysis of ethylene. Although this system is nominally dry because no water vapor was added, a relative humidity of approximately 5% (i.e., 1500 ppm) has previously been measured in this Teflon chamber under dry conditions. Although we cannot state definitively that $HOCH_2OOH$ is the organic hydroperoxide detected, one source of the organic hydroperoxide signal certainly results from the ethylene–ozone system. This was confirmed by performing an experiment mixing ethylene and ozone together in the dark and sampling the effluent. Again the organic component, reported as ROOH in the TTU system, was much greater (a factor of 7) than the inorganic component. The DSFD operates with water as the scrubbing solution. In dilute solution, HMP is expected to hydrolyze to H_2O_2 and HCHO, although the reaction is slow on the time scale of the DSFD operation. The hydrolysis, however, is strongly base catalyzed (*21*). A pH 10 NaOH scrubbing solution was used during one experimental set, and this solution with MnO_2 differentiation, as described above, drastically lowered the observed organic peroxide/H_2O_2 ratio. The organic peroxide concentration decreased by nearly 1 order of magnitude

with a concomitant rise in the observed H_2O_2 concentration. While these measurements do not confirm the presence of HMP, the observations are consistent with known reactivities of HMP.

Evidence has also been presented for the gas-phase formation of HMP in the HCHO oxidation system (*22*, *23*). For this mechanism the precursor $HOCH_2OO$ is formed from the reaction of HO_2 with HCHO. However, in the presence of NO_x, the major products appear to $HOCH_2O-ONO_2$ and formic acid, with no evidence of the formation of HMP (*24*). Thus, while the formation of HMP in the C_2H_4/NO_x system does not appear to be due to the oxidation of HCHO by HO_2, this possibility cannot be completely discounted. Other mechanisms to produce organic hydroperoxides in this system can also be written.

For the ambient measurements in the relatively clean Research Triangle Park, NC, air environment, some scatter in the data was observed (Figure 3) although there appear to be no major systematic errors. Although these mixtures are probably more complex than the photochemical mixtures, the concentration of the individual organic components in the ambient air is far less. Because the deviations from the mean values are greater in the ambient measurements than in the zero air measurements, other uncertainties might have been present. Possible explanations include interferences from compounds not checked in the zero air measurements or larger calibration uncertainties in the ambient measurements due to the generally longer interval between calibrations. A detailed discussion of the results of the individual techniques now follows.

Luminol (NSI-ES). In this study it seemed reasonable to try to shed additional light on some of the questions that have been raised regarding the ability of this technique to selectively and quantitatively measure H_2O_2 (*13*). Several formulations of reagents have been recommended, although the one originally proposed (*13*) was used in this study. With the use of this method, a detection limit of 0.1 μM in the liquid phase was attained. (This corresponds to a 1 ppbv gas-phase detection limit for a 30-L air collection in 10 mL of liquid.)

Measurements of H_2O_2 in zero air illustrate possible limitations of this technique with respect to the detection limit and nature of the interferences. The A series (H_2O_2 in air) generally indicates a positive systematic error with respect to the standard, which could be due to uncertainty in the calibration. In the worst case (at the lowest measured concentration) an error greater than a factor of 2 was observed. Discounting this sample (A2), an uncertainty of 20–30% was generally observed in this series. Sampling periods A3 and A4 were not taken since they would have required longer collection times than the allotted sampling period. The relatively long collection times required represents another limitation of the method as we used it.

The measurements of H_2O_2 in zero air mixtures with added O_3 (sampling periods B3 and B4) did not show significant artifact formation at the levels employed. Although sampling period B2 was not taken, previous experiments in which 30 L of air containing similar levels of O_3 and essentially no H_2O_2 were bubbled in solution yielded an equivalent H_2O_2 concentration of less than 1 ppbv (i.e., the signal was below the 0.1 μM detection limit). The formation of artifacts from O_3 could be related to the exact nature of the solution into which the airstream is bubbled (e.g., the pH of the solution). In these experiments, the collection medium was twice deionized/distilled water at approximately pH 7 (unbuffered).

SO_2 was the only compound for which an interference was observed in the luminol experiment. SO_2 showed a strong negative interference, with 32 ppbv SO_2 in the gas stream, completely removing the signal for 6.5 ppbv H_2O_2 (see sampling period B5). Experiment C1 suggests that 6 ppbv SO_2 yields a negative interference equivalent to 1–2 ppbv H_2O_2 under the sampling conditions employed. To accurately parameterize this value, a number of experiments would need to be performed. However, experiments C5 and C6 with several species present simultaneously (HCHO and SO_2; HCHO, O_3, SO_2, respectively) indicate that complex solution-phase chemistry may be occurring with the soluble components (e.g., a liquid-phase reaction between O_3 and SO_2; *25*).

From the photochemical mixtures, the measurement of H_2O_2 by the luminol technique indicates the presence of interfering species to give apparently high values for H_2O_2. For the CH_3CHO/NO_x irradiation at both short and long residence times, H_2O_2 values were generally 2–3 ppbv higher than all other measurements. However, as indicated by sample G2 (CH_3OOH and H_2O_2 in air), the interference is not likely to be due to CH_3OOH. The presence of greater than 100 ppbv PAN in both cases would suggest this is a possible interference.

A very stong positive interference was observed for the products of the irradiated C_2H_4/NO_x mixture. The apparent concentration of H_2O_2 from the luminol technique was at least 1 order of magnitude higher than the average value from the other three techniques. The component giving rise to this large interference could be the same component giving rise to the large organic peroxide signal (vide supra) observed in the enzymatic techniques.

To summarize measurements of H_2O_2 in zero air with the luminol technique, no interferences were seen in simple mixtures of H_2O_2 for most common atmospheric oxidants (O_3, NO, NO_2, and HCHO). For SO_2, a negative interference was observed. In the photochemical mixtures evaluated with the luminol technique, the possibility of interferences from unknown species needs to be considered. As a result of these factors and its relatively poor sensitivity, ambient measurements were not made with the luminol technique.

TDLAS (Unisearch). Tunable diode laser absorption spectrometry was the only technique employed in this study that measured H_2O_2 in situ (i.e., without transformation into another medium). For mixtures of H_2O_2 in zero air, this technique measured concentrations from 0.1 to 125 ppbv (i.e., over 3 orders of magnitude). For the standards at 0.11 and 0.12 ppbv (Table I, sampling periods A3 and F2), deviations of 36 and 0% were observed, respectively. At a detection limit of 100 ppt, the estimated accuracy is 25%. Overall, for the zero air mixtures, the average deviation from the standard (for all measurements above its detection limit; 19 total) was 14%. An average net deviation of −3% from the standard indicated that essentially no systematic errors were present. The average deviation from the mean values was 9%. For all chemical interferences tested in the zero air mixtures, no positive or negative interfering signals were observed within the random errors. Overall, the estimated accuracy of this technique on the basis of the zero air standards was approximately 20%, which is in agreement with that calculated from the following uncertainties: (1) 10% from the $TiCl_4$ spectroscopic measurement (Unisearch), (2) 2% for the temperature stability of the permeation system, and (3) 5% for the flow measurement of the permeation system.

For the CH_3CHO/NO_x photochemical mixture at short residence time, the Unisearch data indicate no H_2O_2 present above the 0.10 ppbv detection limit. This is con-

sistent with the expectation that negligible amounts of H_2O_2 would be formed in the presence of 10 ppbv NO because of the rapid removal of HO_2 by NO in this system. The data thus indicate no positive PAN interference in the TDLAS technique for this spectral line.

The largest discrepancies among the techniques appear for the two photochemical mixtures at the long residence time (τ = 6.7 h). For the irradiated CH_3CHO mixture, the TDLAS technique yielded an H_2O_2 concentration between those of the two enzymatic techniques, whereas for the irradiated C_2H_4 mixture, the TDLAS measurement for H_2O_2 was higher than both the enzymatic techniques. The H_2O_2 data for these two mixtures thus show no clear systematic discrepancy among the techniques (other than with luminol).

The ambient data for the TDLAS technique are shown in Figure 3. The data show a tendency to be somewhat lower than the mean value (approximately 15%). Since each mean value comprises either two or three data points, little definitive meaning can be ascribed to systematically higher or lower values in this case. However, even more important for the air in which this study was conducted, the 0.10 ppbv detection limit for this technique appeared to be adequate for ambient measurements.

CSFD (NCAR). The continuous-scrubbing, enzymatically mediated fluorescence detection technique demonstrated high sensitivity and a dynamic range of over 3 orders of magnitude. At the value of the lowest standard (0.062 ppbv), the reported value was about 30% high, while at the highest concentration (128 ppbv), the reported value was within 6% of the standard. As shown in Table I, the average deviation from the standard value for all measured samples in the zero air mixture (18 total) was 18%, whereas the average deviation from the mean values was 10%. With respect to the standard values, NCAR data were systematically high by 8% on average. This systematic deviation does not appear to be due to the presence of interferences, since the average deviation for experiments with potential interferences present is 14% with a net deviation of 3%. Although the overall net deviation for the CSFD (8%) was the largest observed among the techniques, it is still much less than the average percent deviation (18.3%). This 8% net deviation may be due to a minor systematic error in the calibration, although this cannot be ascribed with certainty. This technique showed high sensitivity with measurements well below 0.10 ppbv (e.g., sampling period F3). Although no samples were tested below 0.050 ppbv, the detection limit is probably somewhat better than this value judging from the magnitude of the signal at 0.062 ppbv.

For the CH_3CHO/NO_x mixtures at τ = 2.7 h, a signal equivalent to 0.30 ppbv H_2O_2 was observed. Because the system has been designed to produce PAN, O_3, and HCHO in the absence of H_2O_2 (*26*), the source of the signal must be considered. O_3 and HCHO have previously been shown not to interfere with H_2O_2 measurement, while some of the possible minor products in this system such as CH_3ONO_2 and HNO_3 would have been present at low concentrations (<10 ppbv). There exist several possibilities to explain the observed signal. The first is a possible interference due to PAN. (The relative difficulty of generating pure PAN precluded its testing as a single component interference.) If PAN represents an interference for this system that was linear with PAN concentration, the interference as H_2O_2 would represent 0.3% of the gas-phase PAN concentration. Under most atmospheric conditions for which PAN is less than 10 ppb (*27*), the magnitude of the interference would be on the same order as the detection limit for this system, approximately 0.03 ppbv. A second possibility is that H_2O_2 is produced in the reaction chamber. Although the reaction conditions strongly preclude the gas-phase formation of H_2O_2, the possibility of wall formation cannot be discounted. However, the TDLAS does not show evidence for such wall formation within the uncertainty of its detection limit (0.1 ppbv). Other and perhaps more likely possibilities include in situ formation of H_2O_2 in the aqueous sampling medium or the uncertainties associated with measuring H_2O_2 by difference in the presence of a majority of organic hydroperoxides.

In the CH_3CHO photochemical mixture at τ = 6.7 h, the CSFD yields a value higher than either the DSFD or TDLAS values. For the irradiated C_2H_4/NO_x mixture, however, the H_2O_2 concentration from the CSFD technique is significantly lower than all the other data. Although data are not presented, a sizable organic peroxide component was detected by CSFD in both photochemical systems. The variations in H_2O_2 concentrations (with respect to the TDLAS and DSFD techniques) probably reflect normal random uncertainties in the total peroxide signal and the organic component.

As in the zero air and photochemical mixtures, NCAR ambient data were generally high with respect to the mean values by about 25%. It is recognized that the true values are, of course, not known and that the source of this apparent systematic tendency should be investigated further.

DSFD (TTU). This diffusion-scrubbing, enzymatically mediated fluorescence detection technique demonstrated high sensitivity and a dynamic range of more than 3 orders of magnitude. For the lowest standard (0.062 ppbv), the reported value was 13% high. At the upper end (128 ppbv), the reported value (70 + 30/−5) was 45% lower than the standard values. However, the discrepancy was undoubtedly due to the difficulty in obtaining an accurate calibration standard for high levels of H_2O_2. (The calibration source is specifically designed for ambient-level measurements.) For the 17 TTU measurements of H_2O_2 in zero air with and without interferences, the average deviation with respect to the standard H_2O_2 concentration was 21%, while the average deviation from the mean was 16%. The average net deviation was 2% lower than the standard, suggesting that only minor systematic errors could have been present. Of some concern is the 0.8 ppbv signal present with 450 ppbv O_3 and no H_2O_2 in zero air (sampling period B2). This interference appears to be real and reproducible, but techniques have been developed in the TTU laboratories to compensate for this effect. Such compensation was not a part of this study since the mixtures were given blind. The detection limit for H_2O_2 based on these results is better than 0.062 ppbv, and a detection limit of 0.050 ppbv is realistic. (The detection limit based on the signal to noise ratio was 0.020 ppbv.)

The data originally reported for the C series were factors of 2.5 lower than those presented in Table I. However, a subsequent check of the calibration data indicated that the apparent sensitivity of the instrument was 2.5 times greater in series C than in all other series because the calibration solution was 2.5 times more concentrated than originally calculated. To more fairly evaluate the TTU method for precision and accuracy, we have included the corrected data in these tables.

The data for the CH_3CHO/NO_x irradiation at τ = 2.7 h shows a signal equivalent to 0.34 ppbv H_2O_2, which is nearly equivalent to that reported by NCAR. By the same arguments discussed earlier, this interference could be due to PAN or the other possibilities cited. (It should be noted that the PAN concentration in solution is highly dependent

on solution pH, since PAN is known to hydrolyze at high pH.) The TTU system also shows an organic peroxide signal equivalent to 3.2 ppbv. As with the inorganic peroxide, the organic peroxides in the gas phase are not expected to form to any measurable degree in this photochemical system, thus suggesting a possible wall source as the origin.

The TTU data for the photochemical experiments having long residence times (τ = 6.7 h) show sizable discrepancies with respect to the other sets of data. However, the organic component represents 93% of the total peroxide in the CH_3CHO/NO_x mixture at a large exent of reaction and 96% in the C_2H_4/NO_x mixture. Since there is also some question as to the collection efficiency for various organic hydroperoxides, the possibility for large discrepancies is easy to envision. (The DSFD technique collects organic peroxides with a lower efficiency than H_2O_2 because of the lower diffusion coefficients.) However, any correction for collection efficiency would result in a higher concentration of organic component. For the ambient data given in Figure 3 there appear to be no major inconsistencies with the mean values although the data do show a general tendency to be lower than the mean values by about 25%.

Conclusions

Several techniques now exist to selectively measure H_2O_2 in the gas phase with high sensitivity. In this particular study, each of the techniques performed remarkably well, particularly under the time constraints of a rigorous field study. The TDLAS, CSFD, and DSFD techniques demonstrated sufficient sensitivity to perform accurate ambient measurements. The enzymatic techniques showed lower detection limits than the TDLAS technique, although each of the techniques can probably be further optimized. The TDLAS technique showed no observable interference from O_3, PAN, or the other compounds checked. The DSFD technique did show an O_3 interference, although this interference can be easily corrected. The enzymatic techniques were free of interferences for the compounds tested in zero air. The DSFD and CSFD techniques showed an H_2O_2 signal in an irradiated CH_3CHO/NO_x system with sufficient NO to suppress gas-phase H_2O_2 formation. The signal appears to reflect the uncertainty of measuring H_2O_2 in the presence of higher concentrations of organic hydroperoxides. The luminol techniques showed an interference in the presence of SO_2.

The enzymatic techniques also yield the possibility of measuring organic peroxide. Perhaps the most interesting result of this study was the appearance of a large organic peroxide signal in the irradiated ethylene/NO_x system and in the ethylene/O_3 system. Although the existence of the peroxide in these systems cannot be definitively established, the organic peroxide signal was observed in the two systems having different collection methods and discriminating techniques. Although this observation is of significance in itself, it can also lead to increased uncertainty in the H_2O_2 measurements. More experimental work will need to be undertaken to identify the nature and magnitude of ambient organic hydroperoxides and to assess their impact on measurements of ambient hydrogen peroxide concentrations.

Registry No. H_2O_2, 7722-84-1.

Literature Cited

(1) Moller, D. *Atmos. Environ.* **1980**, *14*, 1067–1076.
(2) Bufalini, J. J.; Gay, B. W., Jr.; Brubaker, K. L. *Environ. Sci. Technol.* **1970**, *6*, 816–821.
(3) Kok, G. L.; Darnall, K. R.; Winer, A. M.; Pitts, J. N., Jr.; Gay, B. W. *Environ. Sci. Technol.* **1978**, *12*, 1077–1080.
(4) Lazrus, A. L.; Kok, G. L.; Gitlin, S. N.; Lind, J. A.; McLaren, S. E. *Anal. Chem.* **1985**, *57*, 917–922.
(5) Lazrus, A. L.; Kok, G. L.; Lind, J. A.; Gitlin, S. N.; Heikes, B. G.; Sketter, R. E. *Anal. Chem.* **1986**, *58*, 594–597.
(6) Dasgupta, P. K.; McDowell, W. L.; Rhee, J. S. *Analyst (London)* **1986**, *111*, 87–90.
(7) Hwang, H.; Dasgupta, P. K. *Anal. Chem.* **1986**, *58*, 1521–1524.
(8) Dasgupta, P. K.; Hwang, H. *Anal. Chem.* **1985**, *57*, 1009–1012.
(9) Hwang, H.; Dasgupta, P. K. *Environ. Sci. Technol.* **1985**, *19*, 255–258.
(10) Slemr, F.; Harris, G. W.; Hastie, D. R.; Mackay, G. I.; Schiff, H. I. *J. Geophys. Res.* **1986**, *91*, 5371–5378.
(11) Zika, R. G.; Saltzman, E. S. *Geophys. Res. Lett.* **1982**, *9*, 231–234.
(12) Heikes, B. G.; Lazrus, A. L.; Kok, G. L.; Kunsen, S. M.; Gandrud, B. W.; Gitlin, S. N.; Sperry, P. D. *J. Geophys. Res.* **1982**, *87*, 3045–3051.
(13) Kok, G. L.; Holler, T.; Lopez, M.; Nachtrieb, H. *Environ. Sci. Technol.* **1978**, *12*, 1072–1076.
(14) Lind, J. A.; Kok, G. L. *J. Geophys. Res.* **1986**, *91*, 7889–7895.
(15) Pilz, W.; Johann, I. *Int. J. Environ. Anal. Chem.* **1974**, *3*, 257–270.
(16) Kuntz, R.; Lonneman, W. A.; Namie, G.; Hall, L. A. *Anal. Lett.* **1980**, *13*, 1409–1415.
(17) Fox, D. C.; Stockburger, L.; Weathers, W.; Spicer, C. W.; Mackay, G. I.; Schiff, H. I.; Eatough, D. J.; Mortensen, F.; Hansen, L. C.; Shepson, P. B.; Kleindienst, T. E.; Edney, E. O. *Atmos. Environ.*, in press.
(18) Shepson, P. B.; Kleindienst, T. E.; Edney, E. O.; Namie, G. R.; Pittman, J. H.; Cupitt, L. T.; Claxton, L. D. *Environ. Sci. Technol.* **1985**, *19*, 249–255.
(19) Martin, A.; Barber, F. R. *Atmos. Environ.* **1981**, *15*, 567–578.
(20) Gab, S.; Hellpointner, E.; Turner, W. V.; Korte, F. *Nature (London)* **1985**, *316*, 535–536.
(21) Marklund, S. *Acta Chem. Scand.* **1971**, *25*, 3517–3531.
(22) Su, F.; Calvert, J. G.; Shaw, J. H.; Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. D. *Chem. Phys. Lett.* **1979**, *65*, 221–225.
(23) Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. D. *Chem. Phys. Lett.* **1980**, *75*, 533–535.
(24) Barnes, I.; Becker, K. H.; Fink, E. H.; Reimer, A.; Zabel, F.; Niki, H. *Chem. Phys. Lett.* **1985**, *115*, 1–8.
(25) Maahs, H. G. *J. Geophys. Res.* **1983**, *88*, 10721–10732.
(26) Shepson, P. B.; Kleindienst, T. E.; Edney, E. O.; Nero, C. N.; Cupitt, L. T.; Claxton, L. D. *Environ. Sci. Technol.* **1986**, *20*, 1008–1013.
(27) Temple, P. J.; Taylor, O. C. *Atmos. Environ.* **1983**, *17*, 1583–1587.

Received for review March 9, 1987. Accepted August 10, 1987. Although the research described in this article has been funded wholly or in part by the U.S. Environmental Protection Agency through Contract 68-02-4033 to Northrop Services, Inc.—Environmental Sciences, it has not been subject to the Agency's peer and policy review. Therefore, it does not necessarily reflect the views of the Agency, and no official endorsement should be inferred. Unisearch Associates would like to acknowledge the Coordinating Research Council, Atlanta, GA, and the Electric Power Research Institute, Palo Alto, CA, for financial assistance in constructing the experimental apparatus and in developing procedures to measure H_2O_2.

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

This article documents research that was conducted under the auspices of the U.S. Environmental Protection Agency (USEPA). As an arm of the government, the USEPA has a paid up, non-exclusive, irrevocable, worldwide license to reproduce, prepare derivative works, and distribute to the public all of the material contained herein, and to grant others acting on its behalf the right to do so. The USEPA grants to the National Technical Information Service, Department of Commerce, the right to act as its agent in the distribution of this material.